



# ***High-Temperature Polymer Membranes***

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***Argonne National Laboratory***



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Office of Science Laboratory  
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# ***Project Objectives***

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- **To develop a proton-conducting membrane electrolyte for operation at 120-150°C and low humidities to meet DOE's technical targets**
- **Investigate use of dendritic macromolecules attached to polymer backbones, cross-linked dendrimers, and inorganic-organic hybrids**
  - Measure thermal stabilities and conductivities of samples 11/03✓
  - Prepare and characterize inorganic-organic hybrids 02/04✓
  - Fabricate and test MEAs using high-temperature membranes 09/04

# ***Budget***

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- Total Project Funding,  
FY'02-FY'04: \$700 K
- FY'04 Funding: \$250 K

# ***Technical Barriers and Targets***

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- **This project addresses DOE's Technical Barriers for Fuel Cell Components**
  - E: Distributed Generation Durability
  - O: Stack Material and Manufacturing Cost
  - P: Component Durability
  - Q: Electrode Performance
  - R: Thermal and Water Management
- **DOE's Technical Targets:**
  - High, sustained proton conductivity ( $>0.1$  S/cm) at 120°C and 25% RH (automotive)
  - Low oxygen and hydrogen cross-over (2 mA/cm<sup>2</sup>)
  - Low cost,  $<\$5/\text{kW}$
  - Durability of  $>5,000$  hours
  - Able to withstand temperatures as low as -40°C

# ***Approach: Dendritic macromolecules and Organic/inorganic hybrids***

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- **Dendritic Macromolecules**
  - ✓ Highly branched spherical macromolecules
  - ✓ High surface charge densities
    - *May facilitate high proton transfer with reduced water mediation*
    - *May improve water retention at high temperatures*
- **Inorganic/Organic Hybrids**
  - ✓ Variable charge density and distribution
  - ✓ High thermal and dimensional stabilities
  - ✓ Inorganic component improves water retention at high temperatures

# Safety

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- **Internal safety reviews have been performed for all aspects of this project to address ESH issues**
  - Membrane synthesis
    - *All synthesis is performed in a hood to exhaust vapors of organic solvents (e.g., DMF)*
    - *Used organic solvents are collected and disposed of through the laboratory's Waste Management Operations*
  - Membrane testing
    - *Thermal gravimetric analysis – purge gas exhausted into hood*
    - *Conductivity apparatus – “safe” hydrogen (<4% H<sub>2</sub> in He) is used as a purge gas*
- **Safety reviews are updated and renewed annually**

# ***Project Timeline***

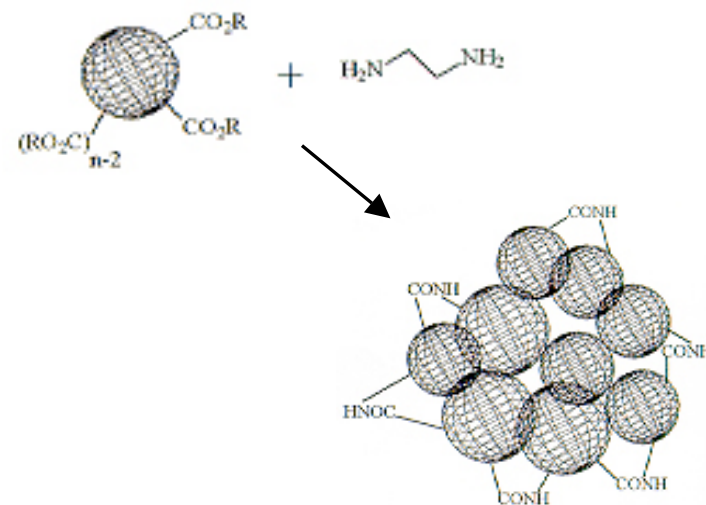
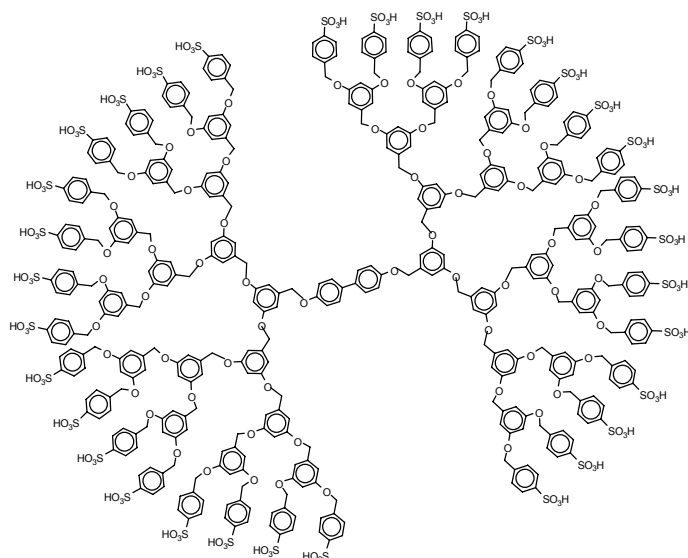
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FY'02			FY'03			FY'04			FY'05		
1	2	3	4	5	6	7	8	9	10	11	12

- 1, 2, 3: Evaluated 3 classes of dendrimers, established capability to measure ionic conductivity, down-selected to one class of dendrimer
- 4, 5, 6: Characterized and measured ionic conductivity of polyarylether hyperbranched membrane, prepared membranes from modified commercial systems (PEO), improved membrane properties
- 7, 8, 9: Measured thermal stabilities and proton conductivities of membranes, improved membrane-forming characteristics of materials, fabricate membrane-electrode assembly from most promising material
- 10, 11, 12: Down-select membrane materials, determine durability under fuel cell operating conditions, modify materials to improve performance

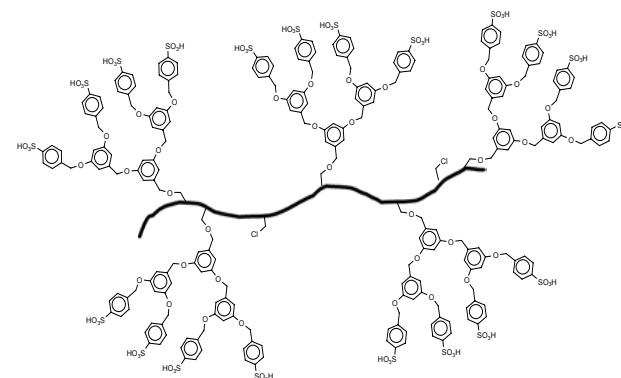
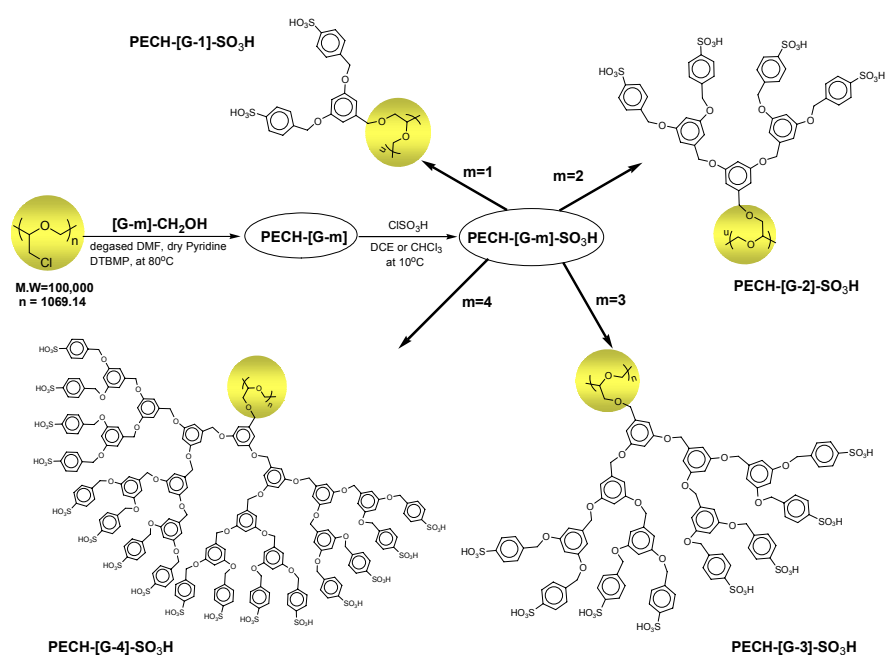
# Dendritic macromolecular membranes

- Aryl ether dendrimers chosen due to high thermal stability
- High density of sulfonate groups imparts water solubility
  - cross-linking eliminates water solubility and controls swelling
  - identity of cross-linker determines pore size and film-forming characteristics
  - attaching dendrimer to polymer backbone is an alternative strategy to eliminate water solubility and allow film formation



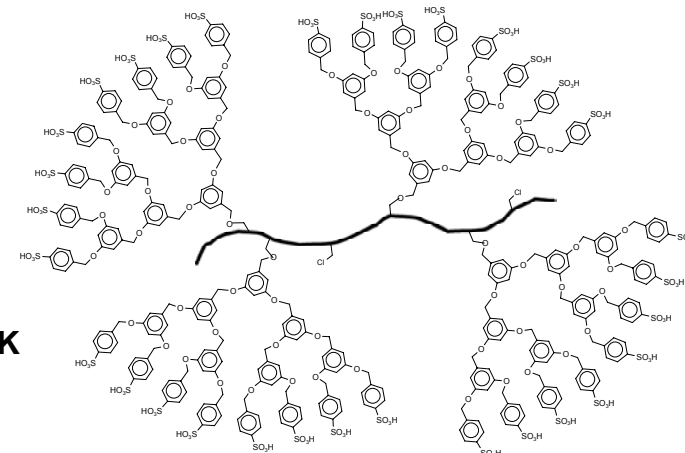


# Dendrimers have been attached to polyepichlorohydrin to form water-insoluble films



**PECH-G2-SO<sub>3</sub>H**

M.W of Polyepichlorohydrin = 100K or 700K

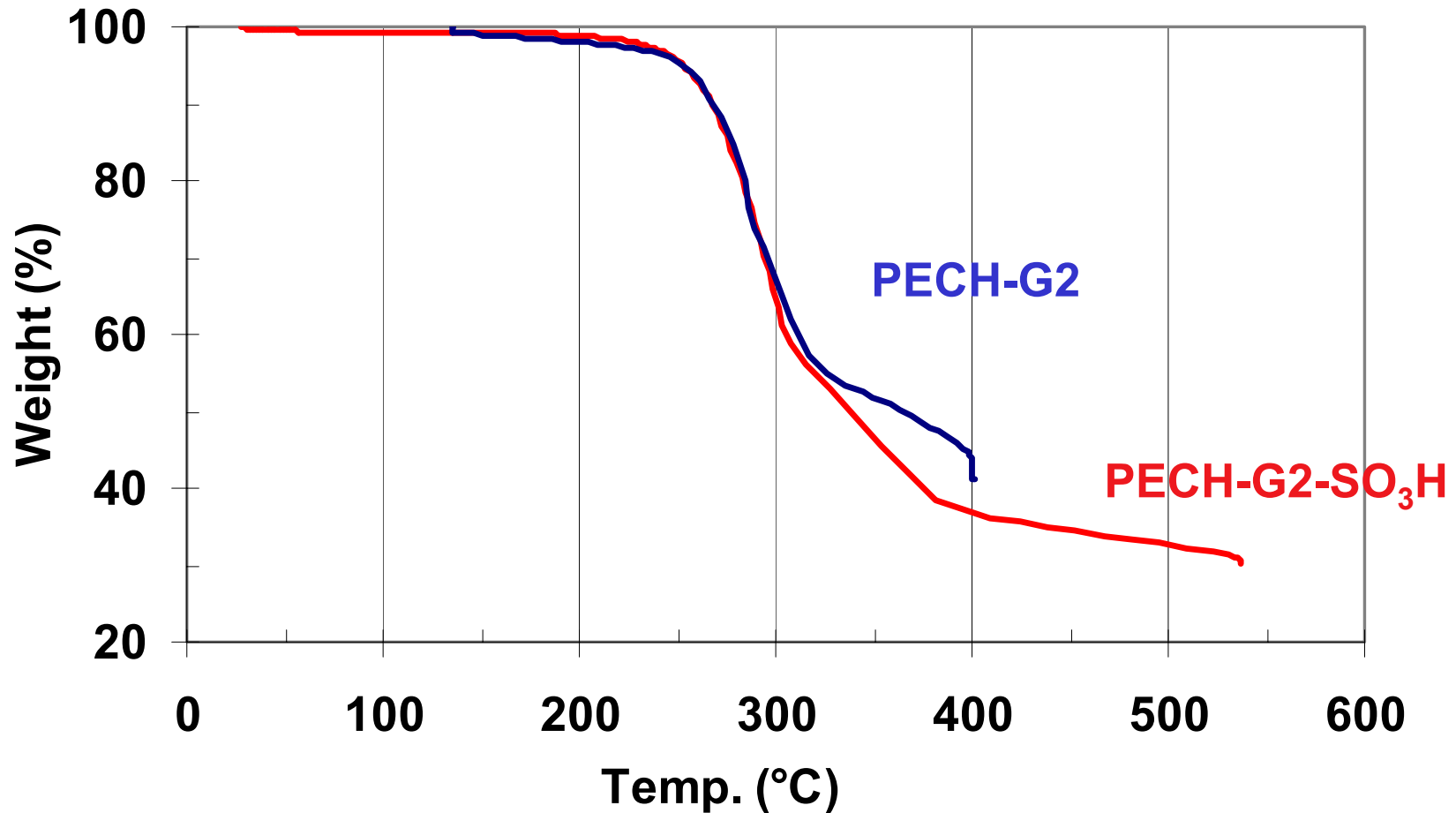


**PECH-G3-SO<sub>3</sub>H**

M.W of Polyepichlorohydrin = 100K

# *TGA shows PECH-G2-SO<sub>3</sub>H polymer is stable up to 190°C*

PECH MW = 100,000



# ***Dendronized polyepichlorohydrin has a high density of proton-conducting groups, but is water insoluble***

- **Acid titration results:**

- PECH-G2-SO<sub>3</sub>H: 4.0 meq/g
- PECH-G3-SO<sub>3</sub>H: 4.05 meq/g
- Nafion: 0.91 meq/g

- **Initial conductivity results for PECH-G2/G3-SO<sub>3</sub>H: (20% G2/80% G3)**

Temperature (°C)	Relative Humidity (%)	Conductivity (S/cm)
21	100	0.031
56	100	0.081
73	59	0.036
98	22	0.022

- **Initial conductivity results for PECH-G2-SO<sub>3</sub>H (MW PECH = 700K):**
  - 0.101 S/cm at 76°C and 6% relative humidity

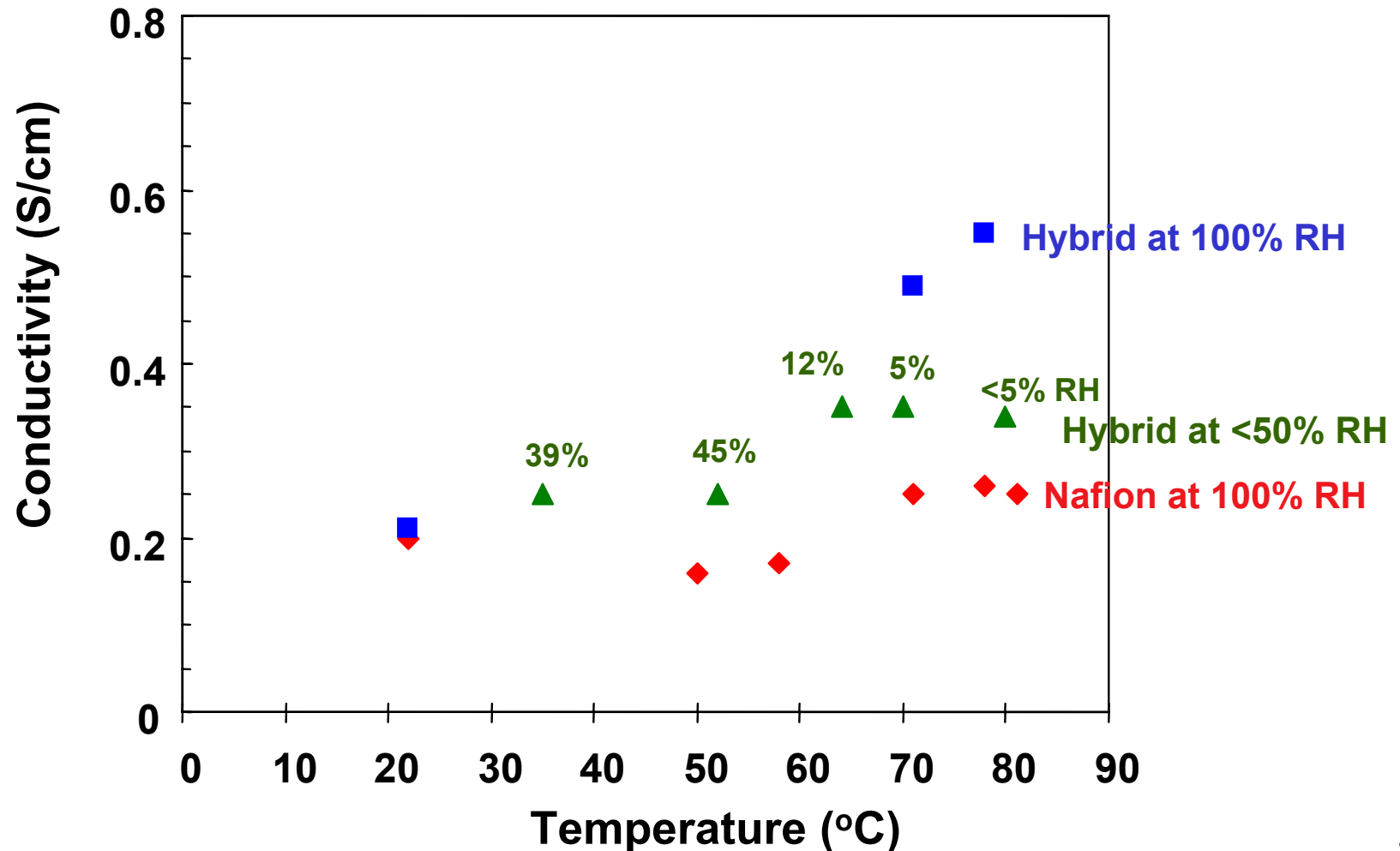
# ***Inorganic-organic hybrid membranes***

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- **Cyclic organic component**
  - high thermal stability ( $>300^{\circ}\text{C}$ )
  - high density of sites for functionalization
  - low cost
- **Sulfonated organic component blended with colloidal silica in formaldehyde to form a gel**
- **Gel is freeze-dried to form an inorganic-organic hybrid material with an equivalent weight of ~600**
- **Initial film formed by blending with Nafion solution (Nafion 70 wt%, Organics 14 wt%, Silica 16 wt%)**

# *Inorganic-organic hybrid has higher conductivity than Nafion in testing up to 80°C*

- Hybrid conductivity was stable through four days of testing



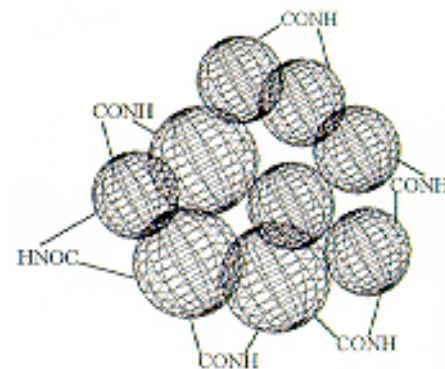
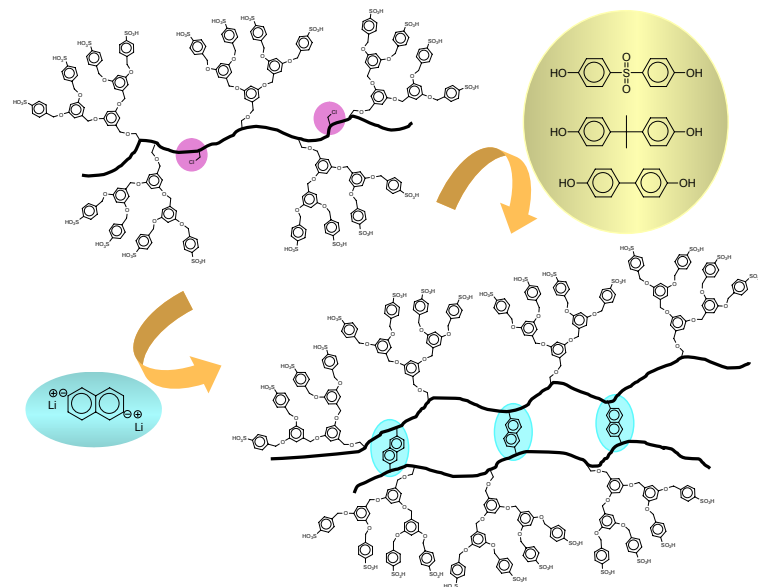
# ***Interactions and Collaborations***

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- Sub-contract with Case Western Reserve University to prepare all-aromatic dendrimers was completed 12/03
- Presentations at International Energy Agency workshops
- U.S. Patent Application 20030035991
- Establishing collaboration with Toyota Motor Corporation

# Future Work

- Complete characterization of G2, G3, and G4 dendritic polymers with PECH (MW = 100K and 700K)
- Cross-link PECH-dendritic polymers to improve mechanical properties
- Cross-link dendrimers to form dendrimeric network
- Develop film-forming techniques for inorganic-organic hybrids that do not rely on Nafion
- Fabricate and test a MEAs using high-temperature membranes



# ***Acknowledgments***

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